

DATA EVALUATION REVIEW 6

I. Study Type: field dissipation (vineyard)

II. Citation:

Mayasich, J.M. and Czarnecki, J.J. Determination of the Leaching Potential and Dissipation of Ignite® Residues. (Glufosinate-ammonium (HOE 039866) and Metabolites (HOE 061517 and HOE 064619) in a California Vineyard. performed by Field Research for Hire, Porterville, CA, and EN-CAS Analytical, Winston-Salem, NC, submitted by Hoechst Celanese Corp., Somerville, NJ. received EPA 6/21/91 under MRID 419201-06.

III. Reviewer:

Typed Name: E. Brinson Conerly-Perks
Title: Chemist, Review Section 3
Organization: EFGWB/EFED/OPP

IV. Conclusions:

- 1) The study is unacceptable.
 - a) The data are too variable. EFGWB does not believe that a meaningful value can be obtained by averaging a set of results such as 0.109 ppm, 0.109 ppm, 0.052 ppm, and <0.05 ppm (four actual "replicate" values).
 - b) The application rate was not confirmed. Soil samples contained only a fraction of the nominally applied material even in bare-ground samples. Moreover, there was poor recovery of applied material analyzed from application cards, especially in the second and third treatments, although the applicant states that a difference in orientation of the cards accounts for these discrepancies.
- 2) Although these data are of extremely limited usefulness in describing precisely the environmental behavior of Glufosinate ammonium, some cautious inferences can be made:

The half-lives determined in the study are remarkably similar for the two study sites, weeded and bare. The compound appears to have a mean half-life of ca. 39 ± 23 days, indicating a certain degree of persistence.

The study did not disclose any detectable residues below the 1 foot depth. This indicates that leaching might not occur under these conditions.



V. Materials and Methods:

Materials

test compound -- Ignite Herbicide containing 200 gm Glufosinate ammonium (1.67 lb ai/gal)

test site -- vineyard in CA, planted with grapes, sandy loam surface soil

test plots -- each 80 x 120 feet, sandy loam surface soil (characteristics included in data following DER)

weed-grown, untreated -- upwind and upslope from treated plots
weed-grown, treated
bare ground, treated

Methods

treatment -- material was applied by boom spray @ 1.5 lb ai/A, on 1/14/88, 5/14/88, and 8/1/88. Additional chemicals [*including paraquat*] applied are listed in attached data

irrigation -- furrow, with sprinkler supplementation when needed to adjust the rainfall to $\geq 120\%$ of the 10 year average

climatic conditions -- monitored daily from CIMIS station located ca. 25 miles NW of the site.

sampling -- 5 types (schedule and details attached):

soil cores
soil spikes
weeds
application cards
spray mixture

extraction

soil cores -- a representative sample of soil was extracted by blending in 0.004 M $\text{Ca}(\text{OH})_2$. The extract was clarified by settling or centrifugation, cleaned up by successive passage through cation and anion exchange resins. The analytes were eluted from the anion column using 10% aqueous formic acid. Water was removed from the eluant by rotary evaporation, and the analytes were derivatized by refluxing for 4-6 hours in a mixture of acetic acid and trimethyl-orthoacetate (TMOA). Excess reagents were removed by solvent exchange into toluene, which was in turn removed by a solvent exchange into methyl acetate.

analysis

derivatized soil extracts -- GC - flame photometric detector with
a 526 nm phosphorous filter

VI. Study Author's Results and/or Conclusions:

ABSTRACT:

Three ground applications of Ignite herbicide were made to each of two plots supporting grapes. One plot contained weeds and the other was bareground. The rate for each of the three applications was 1.5 lb ai/A. An untreated control plot was also included in the study.

The study was primarily designed to evaluate the leaching potential of the parent (HOE-039866) compound and the primary (HOE-061517) and secondary (HOE-064619) metabolites. Even under the worst-case conditions established by the irrigation and cultural practices used in this study (i.e. rainfall + irrigation was 340% of the ten-year average), quantifiable residues were not found below a soil depth of one foot.

The secondary objective of the study was to determine the dissipation rate of the parent and elucidate the formation and decline patterns of the metabolites. Due to the complexity of the study design and the confounding effects of live and dead weed cover, a number of half-life determinations ranging from 11.6 to 69.3 days were calculated. Given the paucity of confounding effects associated with the first application to the bareground plot, the Sponsor considers the corresponding half-life determination of 11.6 days to be the most accurate.

In total, the study provides additional evidence that Ignite herbicide residues are not persistent in the environment and do not tend to leach.

RESULTS AS DESCRIBED BY THE AUTHOR

spray deposition cards -- [results are presented in detail in attachments (table 8)]. The results associated with application one are considered to be adequate validation for an application of 1.5 lb ai/A. The results of applications two and three do not appear to validate this application as directly. However, the sponsor believes that they are adequate due to the following rationale:

- 1) For application one the entire surface of the cards was analyzed, and ... the data were adequate.
- 2) Only 24% of the surface of the cards was analyzed for applications two and three. This resulted in an apparent decrease in collection efficiency of nearly two-fold. Considering the critical relationships between orientation and design of any deposition card and the application equipment used, it is not surprising that this decrease in collection efficiency was not strictly proportional to the associated decrease in surface area analyzed. The decrease in collection efficiency was remarkably precise ... and therefore key to the sponsor's belief that - while all three applications were accurately made at a rate of 1.5 lb ai/A, the surface area of the samples analyzed for applications two and three... [did]... not reflect the accuracy of these applications.

- 3) Calibration data on file corroborate an application rate of 1.5 lb ai/A for all three applications.

field fortifications -- when corrected for procedural recoveries, $83 \pm 17\%$ (HOE-039866), $82 \pm 11\%$ (HOE-061517), and $78 \pm 10\%$ (HOE-064619) of nominal fortified values were recovered. In addition these data provide adequate storage stability data for all three analytes, since storage times ranged from 192 to 577 days. The maximum of the range exceeds the storage time of the actual field samples.

soil core analysis -- details presented in attachments (tables 9 -- 16)

Weedy plot, application 1

At the 0 - 4" level, HOE-039866 mean residues reached a peak at 0.153 ppm 7 days after treatment (d.a.t.), rapidly declined to negligible levels by 29 d.a.t., and remained so through day 119. Maximum levels of HOE-061517 and HOE-064619 occur 7 and 29 d.a.t. respectively. The half-life of HOE-039866 was calculated to be 34.7 days.

At the 4 - 8" level, HOE-039866 mean residue levels peaked at 0.240 ppm 4 d.a.t., declined to just above the limit of quantitation (loq) by 7 d.a.t., and remained below the loq through day 119. The primary metabolite, HOE-061517, had a single residue above the loq at 4 d.a.t. The secondary metabolite, HOE-064619, had a single mean residue level equal to the loq at 29 d.a.t.

In the 8 - 12" soil horizon, a single mean residue level of 0.053 ppm HOE-039866 was detected 7 d.a.t. The remaining mean residue levels of HOE-039866 and all mean residue levels of the metabolites were below the loq. Analysis of deeper soil horizons indicated that HOE-039866 and its metabolites do not leach beyond a depth of one foot.

Weedy plot, application two

In the 0 - 4" soil horizon, a maximum mean residue of 0.214 ppm HOE-039866 was detected 3 d.a.t. After an immediate decline to negligible levels 7 d.a.t., the mean HOE-039866 residues rose to 0.083 ppm at 20 d.a.t., then declined to and remained at negligible levels through 77 d.a.t. The mean residue levels of HOE-061517 also were bimodal, but staggered from that of HOE-039866, with a maximum mean level of 0.114 ppm being detected 77 d.a.t. The mean levels of HOE-064619 rose from 0.086 ppm on application day to about 0.1 ppm 3 days later, then declined and remained negligible from 7 through 77 d.a.t. The half-life of HOE-039866 was calculated to be 17.3 days. The mean residue levels of each analyte never exceeded the limit of quantitation when soil horizons deeper than 0 - 4" were analyzed.

Weedy plot, application three

In the 0 - 4" soil horizon, the mean residue levels of HOE-039866 reached equivalent maxima of about 0.11 ppm 0 and 7 d.a.t., and then gradually declined to and remained at very low levels through 63 d.a.t. The low mean residue levels of HOE-039866 associated with the 3 d.a.t. sampling may again be attributed to heavy weed cover in the subplots samples. The half-life of HOE-039866 was calculated to be 69.3 days. There was no evidence of any analyte leaching beyond the 0 - 4" soil horizon. Therefore the aggregate results of all samples analyzed clearly indicate that residues of Ignite^R did not leach beyond one foot.

Bareground Plot, application one -- *the sponsor feels this portion of the study is most representative of the overall metabolic fate of HOE-039866, reflecting the absence of a key confounding factor (weeds) and also the absence of influence of previous applications of Ignite^R on the soil microflora.*

In the 0 - 4" soil horizon, mean residues of HOE-039866 rapidly declined from a maximum of 0.267 ppm on day 0 to below the loq by 29 d.a.t. and remained so through day 119. mean levels of HOE-061517 increased to a 0.140 ppm maximum 15 d.a.t. and gradually declined to negligible levels by 119 d.a.t. The formation and decline of HOE-064619 is as expected. The half-life of HOE-039866 was calculated to be 11.6 days.

In the 4 - 8" and 8 - 12" soil horizons, considerable levels of both HOE-039866 and HOE-061517 are present 4 d.a.t. These results coincide with the occurrence of precipitation over days immediately following this application. By 7 d.a.t. the mean residue levels of all analytes in all depths analyzed declined to less than quantifiable levels and remained negligible through day 119. The leaching potential of HOE-039866 and its metabolites defined in the weed covered plot as one foot is now verified in the bareground plot.

Bareground plot, application 2

In the 0 - 4" soil horizon gradually increased to a maximum of 0.318 ppm 7 d.a.t., immediately declined to less than the loq 16 d.a.t., then rose slightly and returned to negligible levels by 77 d.a.t. Mean residues of HOE-061517 exceeded the loq once at 31 d.a.t. and then declined to negligible levels by 77 d.a.t. Mean residue levels of HOE-064619 never exceeded the loq. The half-life of HOE-039866 was calculated to be 34.7 days.

In the 4 - 8" soil horizon, a single mean residue of HOE-039866, barely above the loq is the only evidence of leaching associated with this portion of the study.

Bareground plot, application 3

In the 0 - 4" soil horizon, mean residues of HOE-039866 gradually declined from a maximum of 0.168 ppm on application to negligible levels 16 and 29 days later. The mean level increased slightly to 0.065 ppm 42 d.a.t. and then declined to below the loq 63 d.a.t. The mean residue levels of HOE-061517 remained very low until a maximum of 0.078 ppm was reached 42 d.a.t. by 63 d.a.t. the mean level of HOE-061517 declined to slightly above the loq. Mean residue levels of HOE-064619 never exceeded the loq. a half-life of 69.3 days was calculated for HOE-039866.

In the 4 - 8" horizon, very low levels of HOE-039866 and HOE-061517 were detected 63 d.a.t. Analysis of deeper horizons collected 63 d.a.t. did not detect any analyte at a mean residue level above the loq.

CONCLUSIONS OF THE AUTHOR

The irrigation and overall cultural practices, specific to this study, defined a worst-case scenario for evaluating the leaching potential of Ignite herbicide residues. For example, it should be emphasized that total precipitation (rainfall + irrigation) for the study was 340% of the ten year average. The results indicate that HOE-039866 and its metabolites (HOE-061517 and HOE-064619) are not mobile beyond a depth of one foot.

A key factor which tended to confound the dissipation results of the study was weed cover. This cover was represented by live weeds in one treated plot and dead weed trash in the other treated plot. The plot with live weeds was included in the study to represent the use scenario for Ignite herbicide as a component of a typical herbicide program for vineyards. This cover was of sufficient density to intercept considerable quantities of test material by the time the second and third applications were made. A significant source of test material therefore remained poised for introduction to the soil matrix upon any precipitation or irrigation event. The half-life calculations associated with applications two and three are, therefore, considered to be semi-accurate. The most accurate estimation of the half-life of HOE-039866 was calculated to be 11.6 days (Application I, Bareground, 0-4" soil)

VII. Reviewer's Comments:

The data are too variable to establish a pattern of disappearance of parent and appearance and disappearance of degradates. The variability inherent in field work does not appear to account for values as divergent as 0.2 ppm and <0.05 ppm (non-detect) in a cohort of samples which are supposed to be replicates. It is unacceptable to take such imprecise data and use the mean as the "correct" value.

The actual application rate claimed is not supported by available data. The highest observed level in soil samples from the bare-ground study (ca. 0.27 ppm in a 4" soil layer) is far below the nominal application rate (0.75 ppm for a 6" soil layer). Also, application card data is less than convincing in establishing the actual application rate, although the applicant has supplied a rationale for those results.

The study results imply that detectable residues of Glufosinate ammonium and its metabolites do not appear lower than one foot below the soil surface.

The data do not define a reliable half-life value, but may be useful for establishing an order of magnitude for the half-life. The data are consistent with a certain amount of persistence. Despite the highly variable data, the author-calculated results from the two plots are remarkably similar. Indeed, two of the three half-life values (for treatments 1, 2, and 3) are identical for both plots, although they do not occur in the same sequence in the two cases. For the weedy plot the value of the $t_{1/2}$ is 40.43 ± 20.61 days, and for the bare ground plot, it is 38.53 ± 23.71 days. The two plots combined give a $t_{1/2}$ of 39.48 ± 22.71 days.

The monitoring of climatological conditions from 25 miles away is insufficient. Particularly in hilly country such as typical grape-growing areas, micro-climates can differ greatly in only a short distance.

VIII. CBI Information Addendum: attached